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AFRPL-TR-65-14

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**(U) EXPERIMENTAL EVALUATION OF HYBALINE B<sub>3</sub>**

**BY**

**V. A. MOSELEY**

**K. E. NIDIFFER**

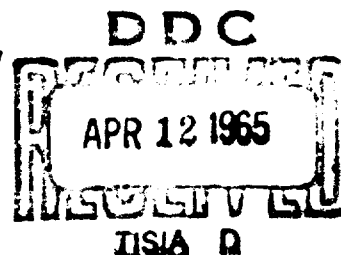
**J. P. FRANKLIN**

**A PAPER PRESENTED TO  
THE SIXTH LIQUID PROPULSION SYMPOSIUM,  
LOS ANGELES, CALIFORNIA,  
25 SEPTEMBER 1964**

**TECHNICAL REPORT NUMBER AFRPL-TR-65-14**

**JANUARY 1965**

**AIR FORCE ROCKET PROPULSION LABORATORY  
RESEARCH AND TECHNOLOGY DIVISION  
AIR FORCE SYSTEMS COMMAND  
UNITED STATES AIR FORCE  
EDWARDS, CALIFORNIA**



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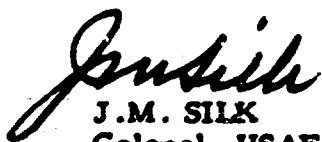
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## FOREWORD

This report covers certain experiments conducted for the evaluation of Hybaline B<sub>3</sub>. It was presented as a paper to the Sixth Liquid Propulsion Symposium, Los Angeles, California, 25 September 1964. It represents work done under Project 314803301, at the Air Force Rocket Propulsion Laboratory, from February 1964 through 15 September 1964. The test work on Hybaline B<sub>3</sub> is continuing, and additional reports will be published by AFRPL.

This report has been reviewed and approved.



J.M. SILK  
Colonel, USAF  
Director, AF Rocket  
Propulsion Laboratory

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**ABSTRACT**

(C) Methylamine beryllium borohydride, produced by Union Carbide Chemicals Company and code-named "Hybaline B<sub>3</sub>", has been subjected to 28 test firings in a nominal 100-pound-thrust uncooled rocket engine. Eleven tests were made with N<sub>2</sub>O<sub>4</sub>, and the remainder were conducted with 90 wt. % H<sub>2</sub>O<sub>2</sub>. Delivered performance with both oxidizers has been low, 82 to 84 percent of theoretical specific impulse. Thermal instability of Hybaline B<sub>3</sub> has been observed; however, changes in composition over a year period are negligible. Hybaline B<sub>3</sub> is compatible with standard materials, and although it is pyrophoric, it presents few handling problems other than toxicity.

(Confidential Abstract)

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## EXPERIMENTAL EVALUATION OF HYBALINE B<sub>3</sub>

### INTRODUCTION.

(C) An experimental program to determine the performance and physical characteristics of Hybaline B<sub>3</sub> is being conducted at the Air Force Rocket Propulsion Laboratory (AFRPL). Hybaline B<sub>3</sub>, made by Union Carbide Chemicals Company under Contract AF 04(611)-8164, is methylamine beryllium borohydride. Table I outlines the physical properties of B<sub>3</sub> as reported by Union Carbide (1). The interest in this new fuel is emphasized by its attractive theoretical performance: 338.4 seconds with N<sub>2</sub>O<sub>4</sub> and 329.5 seconds with H<sub>2</sub>O<sub>2</sub> (1000 psi chamber pressure expanding to sea level;  $\Delta h_f = 0.9$  kcal/mol for B<sub>3</sub>).

(C) Three major factors influence the ultimate use of Hybaline B<sub>3</sub>. These are its toxicity (13 per cent beryllium), its storability, and its dependence on the BN reaction for high performance with N<sub>2</sub>O<sub>4</sub>. This paper presents experimental work on the last two factors and test results with 90% H<sub>2</sub>O<sub>2</sub>.

TABLE I

### (C) PHYSICAL PROPERTIES OF HYBALINE B<sub>3</sub> LIQUID ROCKET FUEL

Name	Methylamine Beryllium Borohydride
Structural Formula	$\text{CH}_3\text{NH}_2:\text{Be}(\text{BH}_4)_2$
Empirical Formula	$\text{BeB}_2\text{CH}_3\text{N}$
Molecular Weight	69.75
Density, gm/cc at 20°C (a)	0.641, 0.650
Vapor Pressure, mm Hg at 25.8°C (b)	1.5
Freezing Point, °C (a)	-11.5, -14

(a) High and low results for fuel shipped from Blue Creek Production Facility.

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Table I (Cont'd)

Viscosity, cp 20°C	3.4
Flash Point, °F (b)	68
Auto Ignition Temperature, °F (b)	284
Surface Tension, dynes/cm (b)	28.6
Specific Heat, cal/gm 20°C (b)	0.6246
Boiling Point, °C	270
Critical Temperature, °C	500
Air Sensitivity	Oxidizes slowly in dry air without ignition
Shock Sensitivity (c)	120.0

## DISCUSSION.

(U) Engine Test System. The basic test article for this propellant is an uncooled rocket engine designed for 100 pounds thrust at 300 psi chamber pressure, three engine configurations have been used. These assemblies are described in Table II. Hardware is interchangeable between these configurations. Figure 1 pictures the 198P engine.

TABLE II

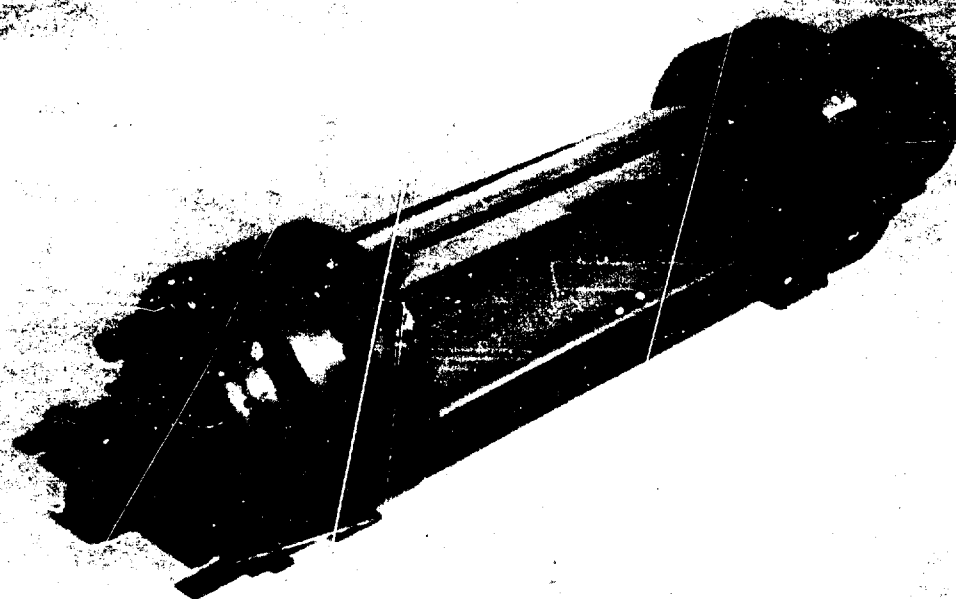
### (U) ENGINE CONFIGURATIONS

<u>No.</u>	<u>Chamber</u>	<u>L<sub>c</sub>, in.</u>	<u>Nozzle</u>
198S	2.5 x 10 in. Stainless Steel	198	Copper D <sub>t</sub> = .56, e = 4.2
198P	2.5 x 10 in. Acrylic Resin	198	
297S	2.5 x 15 in. Stainless Steel	297	

- (b) These tests were made on samples prepared in the laboratory and the values will be redetermined for fuel produced in the Pilot Plant.
- (c) Limit of detection by Olin Mathieson drop weight tester, LPFA Test Method No. 4, LPFA, December, 1959.

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(U) Figure 1. 198P Engine

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Two types of injectors have been tried to date: a "splash plate" design shown in Figure 2, and a conventional  $60^\circ$  included-angle triplet shown in Figure 3. All of the data presented here is from the splash-plate type. Data from the triplet is not available at this time.

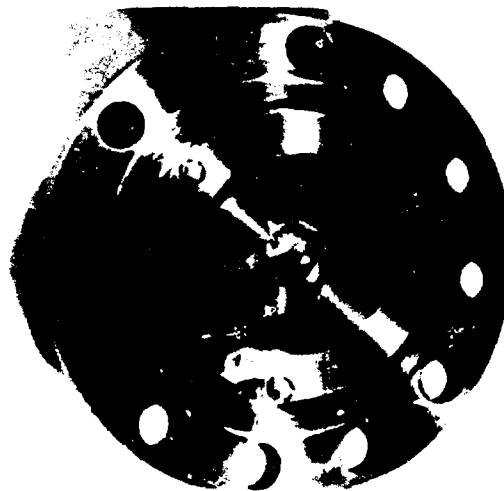
The test system was of simple pressure-fed design. It is shown schematically in Figure 4.

(U) Instrumentation. Chamber pressure, thrust, and set-up pressures were measured with strain gage type transducers, and primary data were recorded on FM tape. Turbine flowmeters were used. All primary data channels, with the exception of the flows, were calibrated end-to-end prior to each day of testing. Although no precision or accuracy program was done on this system, an accuracy of  $\pm 2\%$  is postulated based on studies of a similar system <sup>(2)</sup>. The major source of instrumentation error is the flow measurement. The flexured parallelogram thrust stand is shown in Figure 5 with a 198S engine firing  $B_3/90\% H_2O_2$ .

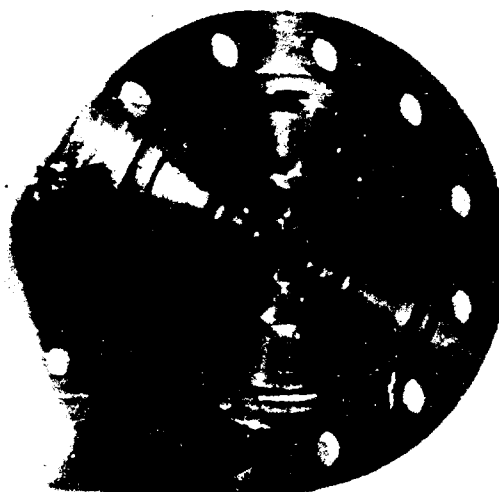
(U) Data Analysis and Correction. Data presented represents average values obtained from time slices taken from 2 to 5-second test firings during steady-state operation. These averages are taken for each test, but no averaging of data from different tests is done.

(U) In order to minimize data corrections, all values are reported normalized to a chamber pressure of 300 psia expanded to 13.2 psia. These conditions were chosen because they are very near the actual test case and they limit the  $I_{sp}$  correction to less than 1%. No corrections for heat loss or the  $15^\circ$  nozzle divergence are included.

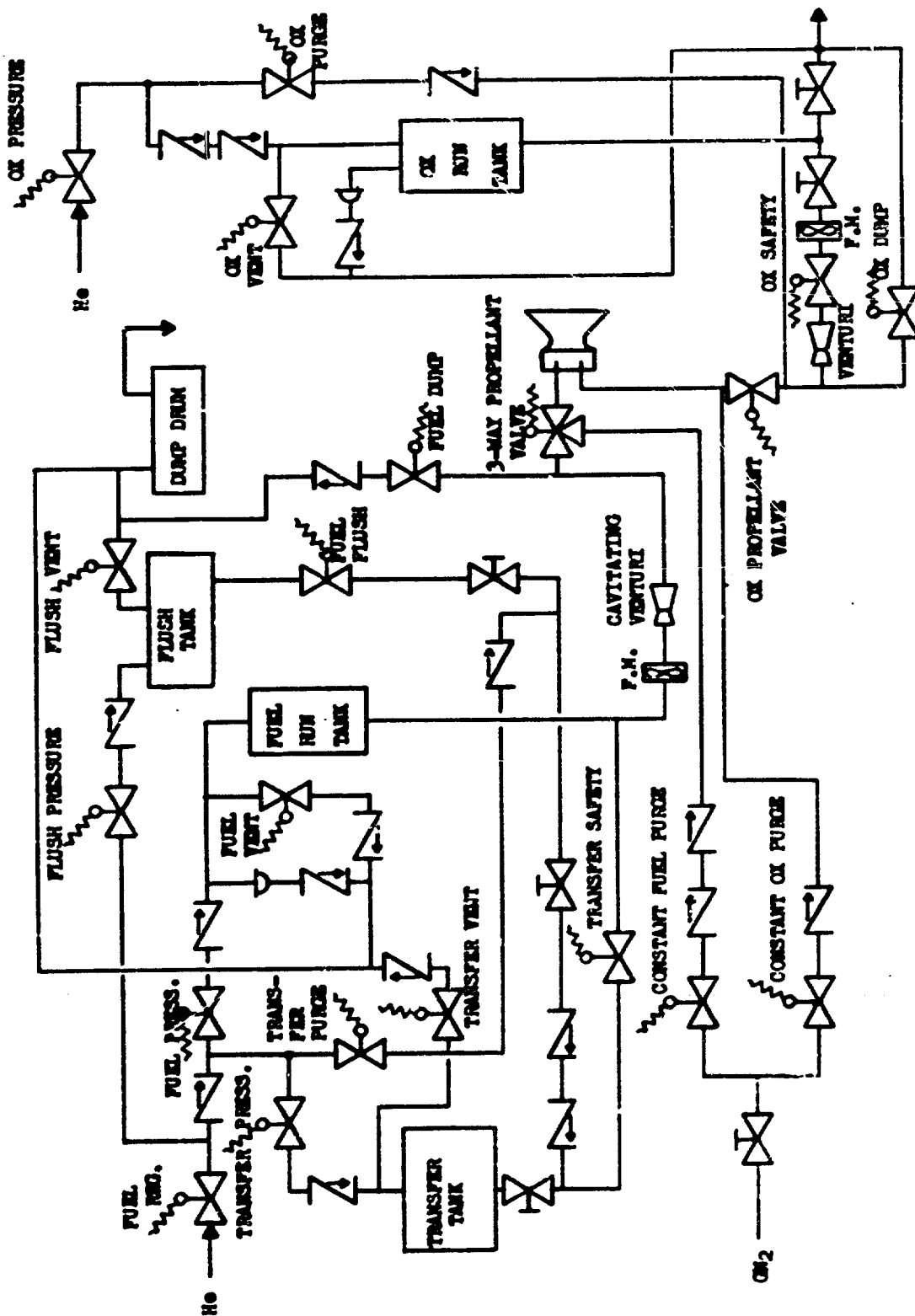
(C) Ignition. Hybaline  $B_3$  is hypergolic with both  $N_2O_4$  and  $90\% H_2O_2$ . As a precaution, however, initial  $H_2O_2$  tests were run with the 198P engine using the cast acrylic resin chamber to minimize the hazard of a hard start. No overpressures were observed on start. But one point of interest is the "chugging" observed during the first 250 milliseconds of the  $B_3/H_2O_2$  tests. Cavitating venturis used for flow control isolated this phenomenon to the



(U) Figure 2. Splash-Plate Injector

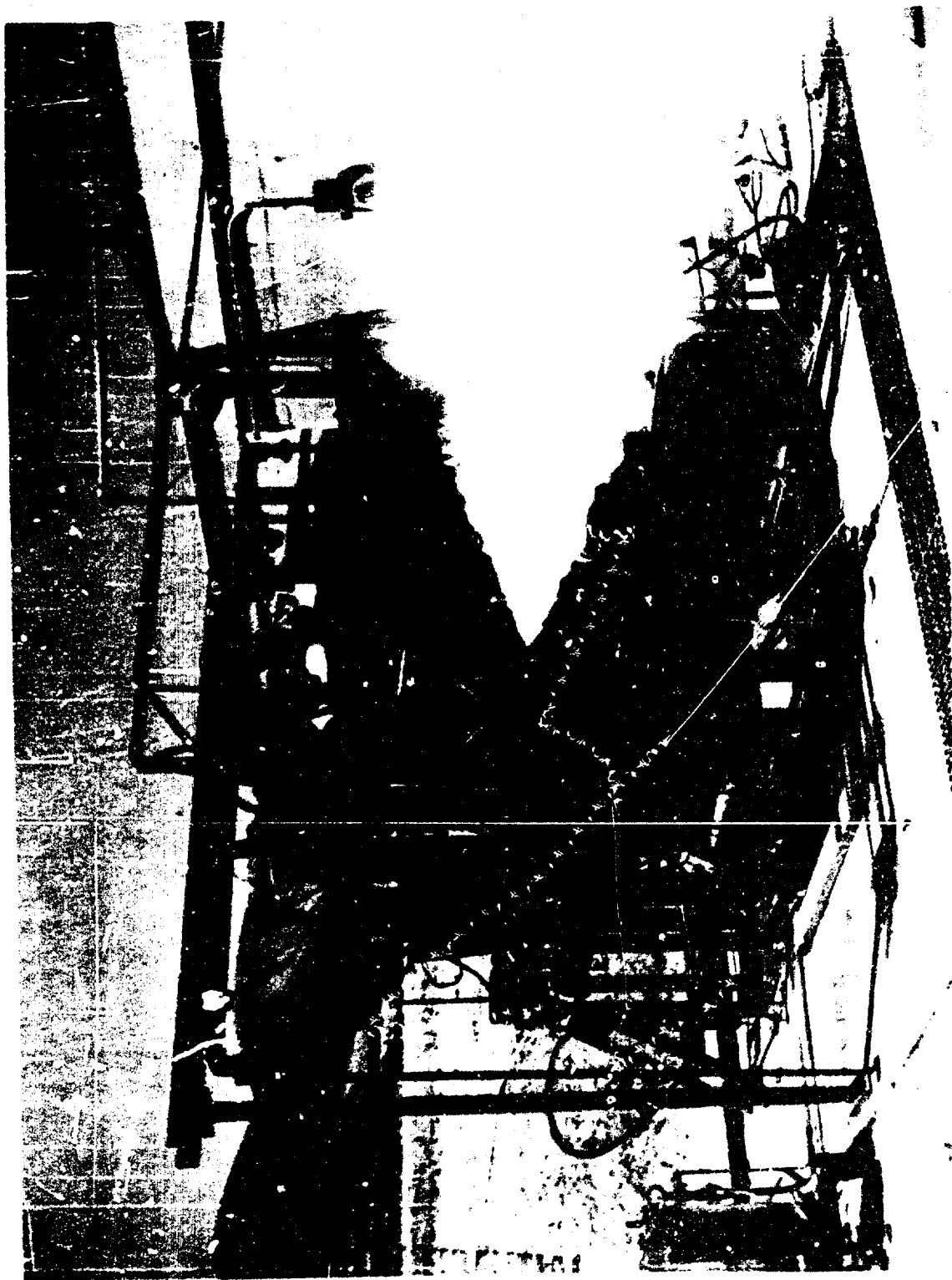


(U) Figure 3. Triplet Injector



(U) Figure 4. Propellant Engine System

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(U) Figure 5. Hybaline B<sub>3</sub> Test System

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thrust chamber and injector. This should be of academic interest only to all except those who require unusually short start transients.

(C) Performance with  $N_2O_4$ . Eleven test firings were made with Hybaline  $B_3/N_2O_4$  during March 1964. This testing was limited by the small quantity, 9.8 pounds, of Hybaline  $B_3$  available then. The splash-plate injection technique was selected on the basis of its relatively good performance with other Hybalines (3, 4).

(C) Six tests were made with the 198S engine. The measured  $I_{sp}$  performance peaked at 237 seconds at an O/F ratio of 1.0. A second splash-plate injector was designed adjusting the injection velocities in an attempt to shift the performance peak to an O/F of 0.5 to 0.6, the theoretical BN reaction region. No difference in the performance of these two injectors could be measured.

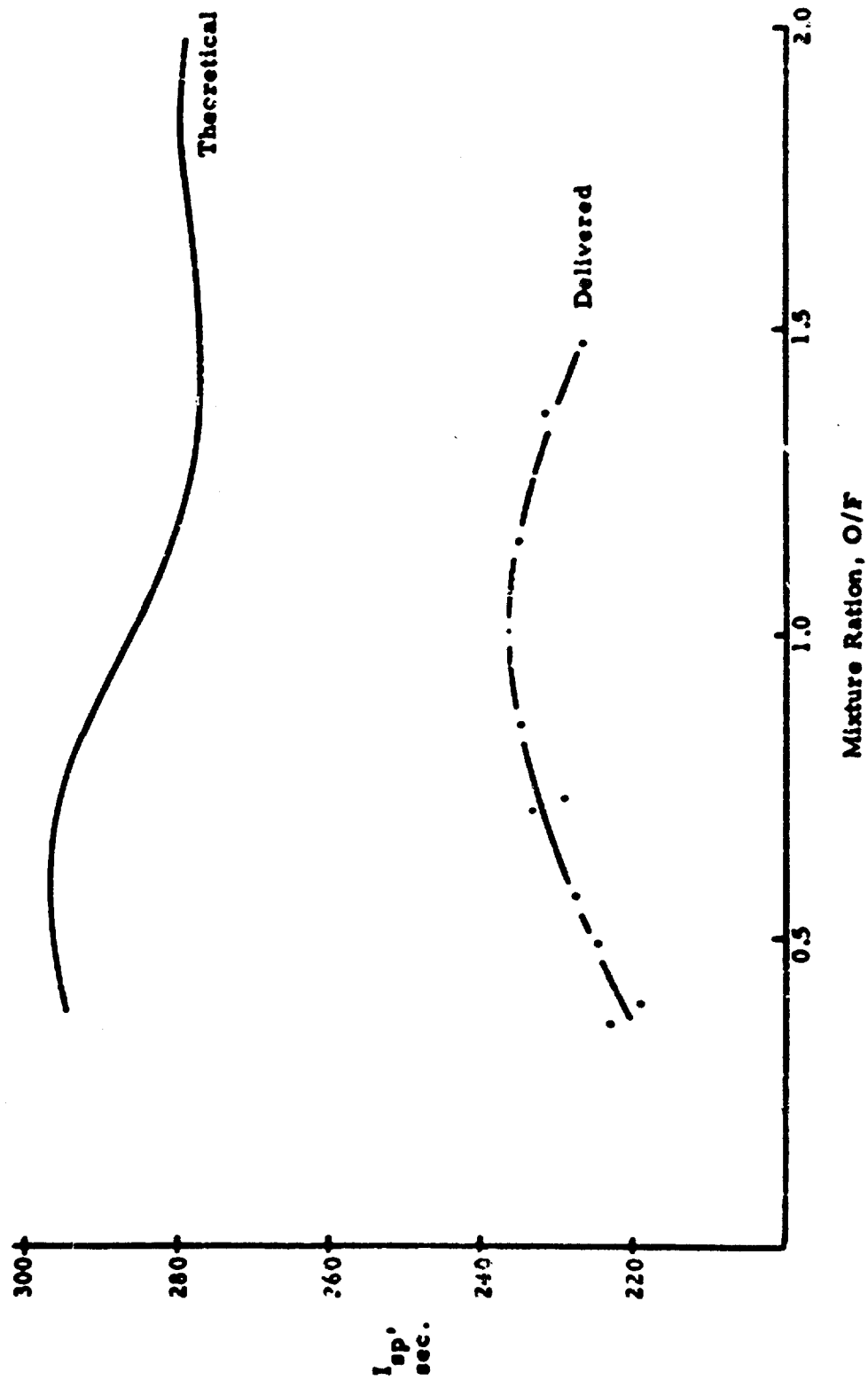
(C) A second attempt to get the BN reaction by increasing characteristic chamber length also proved unsuccessful. Two tests with the 297S engine and the splash-plate injector produced data identical to the 198S configuration.

(U) Reduced  $I_{sp}$  data for the  $B_3/N_2O_4$  tests are plotted and compared to theoretical predictions in Figure 6.

(C) Performance with 90%  $H_2O_2$ . Fourteen test firings were conducted for performance data with Hybaline  $B_3/H_2O_2$  (90 wt. %) during August 1964. The total weight of Hybaline  $B_3$  expended was 8.9 pounds. A splash-plate injection technique was used with a 198S engine. Performance was consistently low in the region of maximum theoretical  $I_{sp}$  and was still increasing at a mixture ratio of 2.3. Table III is a tabulation of the reduced performance data, and Figure 7 is a plot of the  $I_{sp}$  data.

(C) Splash-plate injectors with this engine have normally not been sensitive to design changes such as injection velocity. Therefore, to check for injector effects, the triplet injector was tested. Unfortunately, plugging in the fuel system negated the usefulness of the data from the three tests run. Tests with the triplet will be repeated in October.

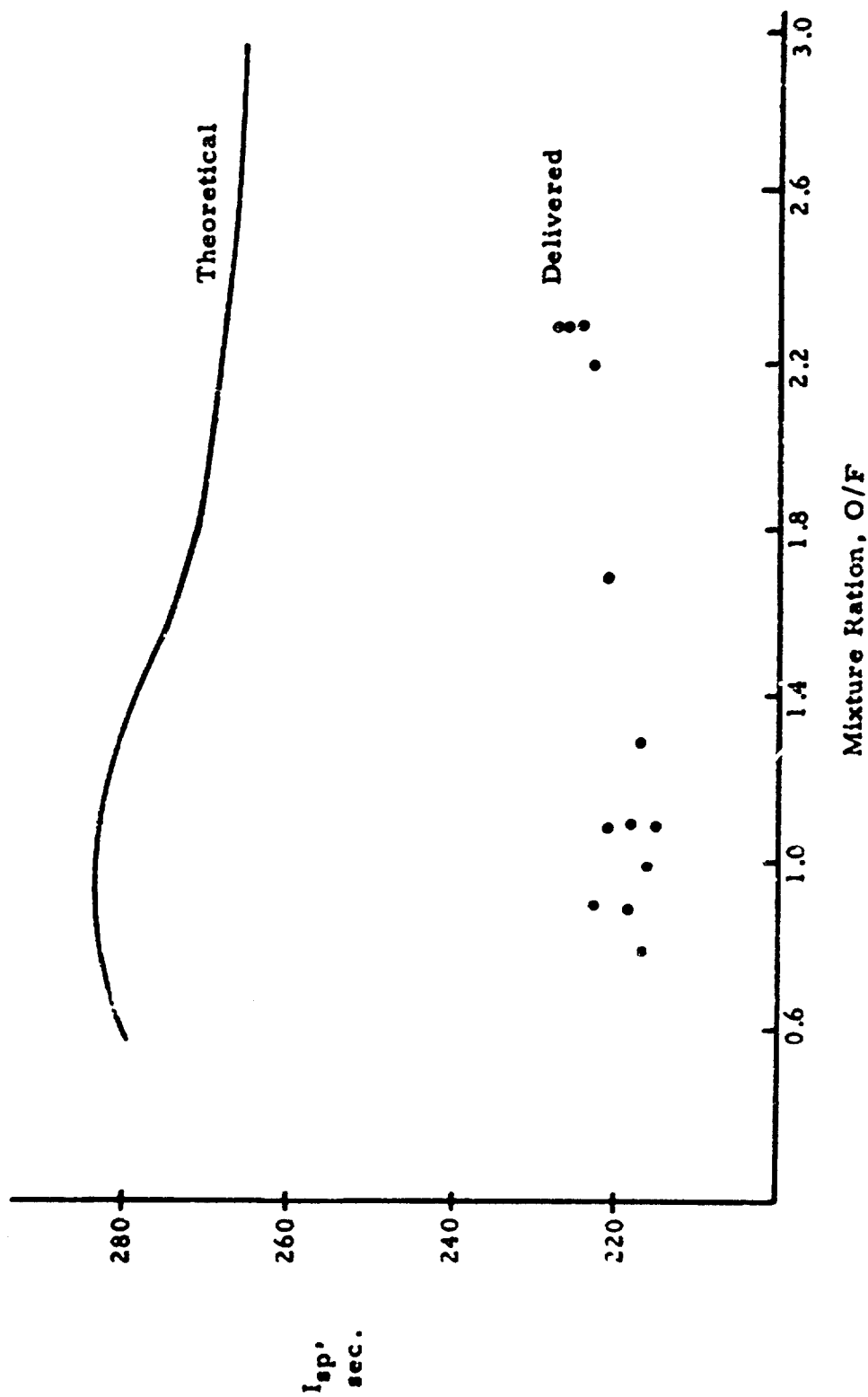
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(C) Figure 6. Performance of Hybaline  $B_3/N_2O_4$ , 300/13.2 psia

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(C) Figure 7. Performance of Hybaline B<sub>3</sub>/90% H<sub>2</sub>O<sub>2</sub>, 300/13.2 psia

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(C) Table III. Reduced  $B_3/H_2O_2$  Data

Run No.	O/r	$I_{sp}$ lb/lb/sec	$I_{sp}$ Corr. lb/lb/sec	C*	F	$P_c$ psia	% $I_{sp}$	% C*
B-34	2.0	222	222	5280	95	293	83	85
B-35	2.3	224	225	5287	96	297	84	86
B-36	2.3	224	224	5278	97	300	84	86
B-37	2.3	225	226	5130	98	300	84	84
B-38	1.7	217	220	5000	90	280	79	82
B-39	0.9	220	222	5460	89	277	78	88
B-40	1.1	214	214	5550	87	297	76	83
B-41	1.0	214	215	5200	86	284	76	85
B-42	NO DATA							
B-43	0.8	212	216	5100	87	265	76	82
B-44	0.9	217	217	5280	93	293	77	85
B-45	1.0	219	220	4948	95	289	78	79
B-46	1.1	217	218	4808	94	290	77	78
B-47	1.3	214	216	4725	91	283	77	77

NOTE: The average buildup of a 0.009-inch oxide crust on the throat of the nozzle complicated throat area measurements and hence C\* calculations.

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(C) Thermal Stability. Union Carbide Company personnel, who are studying the stability of Hybaline B<sub>3</sub>, provided the preliminary stability information presented here <sup>(5)</sup>. Their data, which correlates well with pressure samplings at AFRPL, indicates an inherent instability which produces a pressure rise of 0.06 psi per hour at 122°F and 75% ullage. Tables IV and V show results from one year of storage of Hybaline B<sub>3</sub>.

TABLE IV

(C) THERMAL STABILITY OF HYBALINE B<sub>3</sub>,  
CYLINDER 2, AFTER 1 YEAR OF STORAGE

Ullage	75%	25%	10%
Temp., °F	122	100	100
psi/day	1.2	1.7	8.4

TABLE V

(C) ANALYSIS OF HYBALINE B<sub>3</sub>,  
CYLINDER 2, AFTER 1 YEAR OF STORAGE

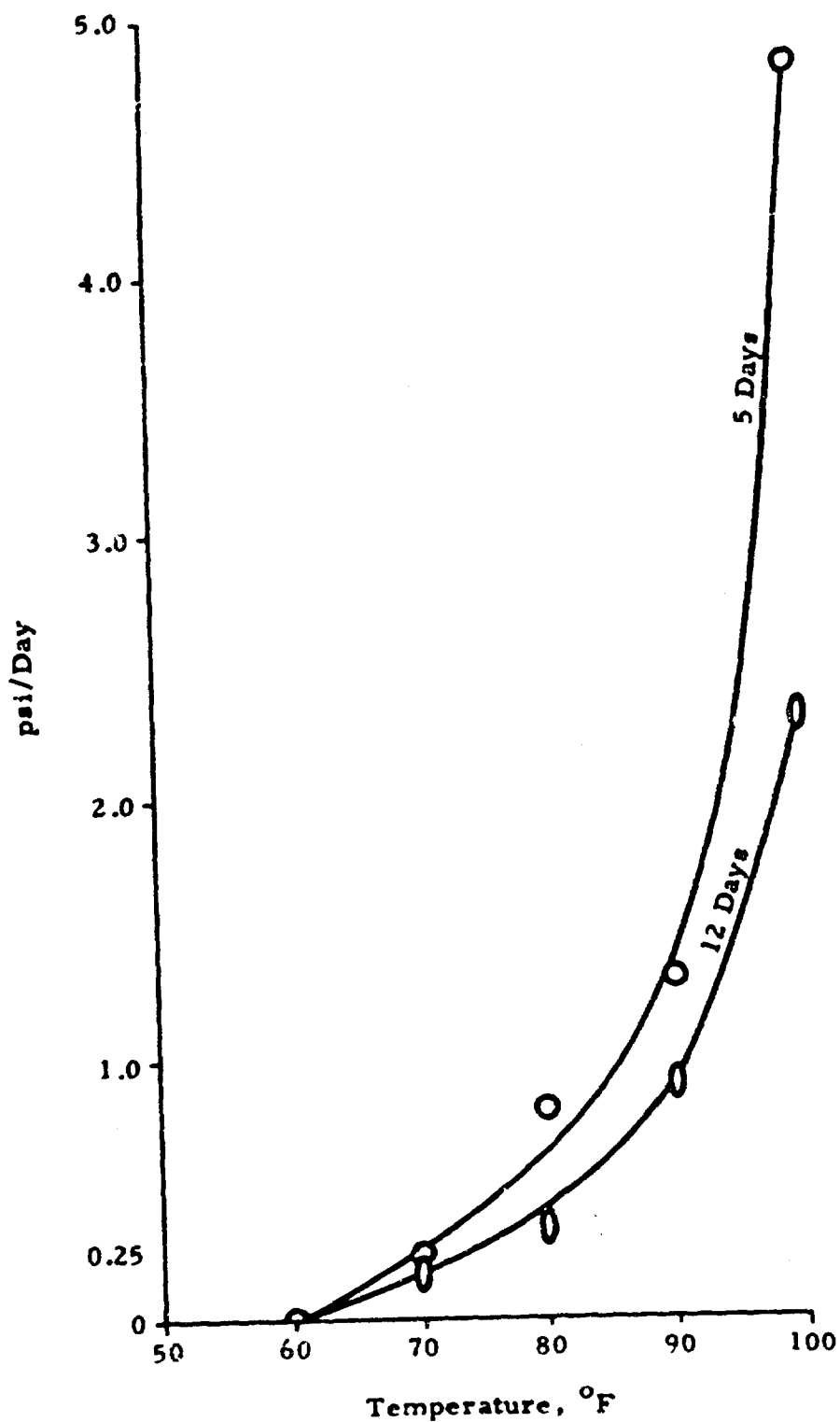
	Theory	As Made	After 1 Year
% B <sub>e</sub>	12.92	12.75	12.74
% N <sub>2</sub>	20.08	19.81	19.64

(C) Variations from batch to batch have been observed. Pressure rises from 3.12 to 12.0 psi/day (100°F, 25% ullage) have been measured. Union Carbide attributes accelerated decomposition to an excess of amine or an incomplete equilibrium reaction. They have been successful in minimizing this variation, and it does not appear to be a serious problem.

(C) Stability of Hybaline B<sub>3</sub> improves markedly below 90°F. Figure 8 shows the effect of temperature on pressure buildup. Figure 9 compares Hybaline B<sub>3</sub> stability to various Hybaline A fuels.

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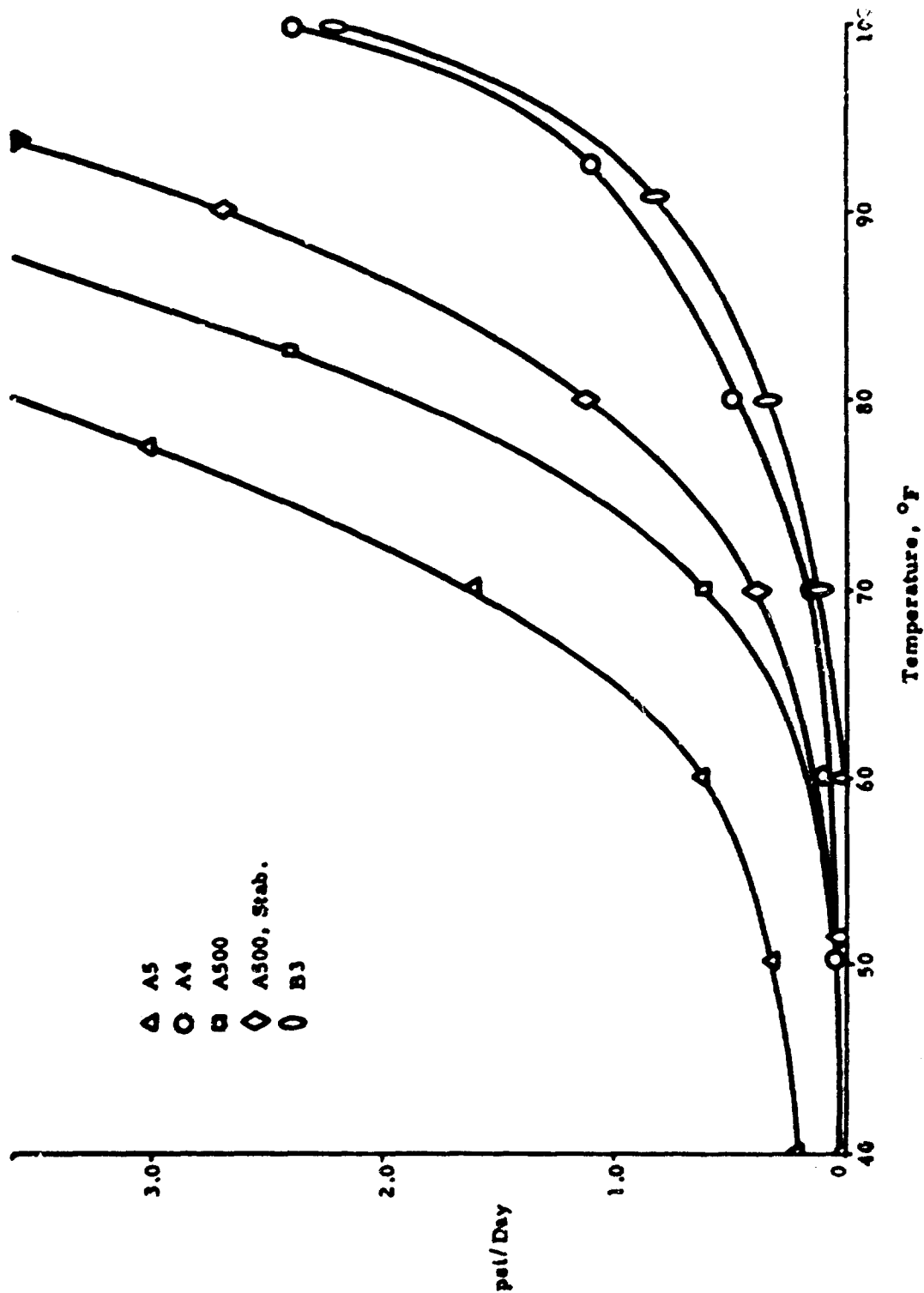
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(C) Figure 8. Storage Stability of Hybaline B<sub>3</sub>, 25% Ullage

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(C) Figure 9. Storage Stability, 25% Ullage

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(C) Handling and Compatibility. We have made 28 test firings with Hybaline B<sub>3</sub> without containment or scrubbing of the exhaust. After each day of testing, the test stand was thoroughly washed with water. The maximum beryllium concentration we have detected after this water wash is 0.2 µg per cubic meter, an order of magnitude below our established in-plant maximum allowable.

(U) Although Union Carbide reports that Hybaline B<sub>3</sub> "oxidizes slowly in dry air" (1), we have found it to be pyrophoric even with the relatively low-humidity air at AFRPL. The exclusion of air and moisture in the test system is essential to prevent formation of hard oxides which can plug valves and lines and bind flowmeters.

(C) We have used benzene as a solvent and system flush for B<sub>3</sub>. Toluene was used also but formed a buttermilk-like substance which adhered to the lines and tank and was extremely difficult to remove. We have not identified this substance yet, but intend to investigate this and the possibility of the formation of soluble beryllium compounds. The soluble compounds are believed to be most toxic, although no official delineation between toxicity of beryllium compounds has been accepted.

(U) We have not undertaken a materials compatibility program, per se, with Hybaline B<sub>3</sub>. Compatibility with stainless steel and Teflon, the materials of construction for our test system, is excellent. We do not anticipate compatibility problems with standard materials with the exception of copper and brass.

### SUMMARY.

(C) Preliminary data from test firings of Hybaline B<sub>3</sub> with N<sub>2</sub>O<sub>4</sub> and with 90% H<sub>2</sub>O<sub>2</sub> shows relatively low delivered performance. Table VI compares delivered I<sub>sp</sub> for various propellants tested in similar engines. This comparison is presented with reservations because the numerous details varied from program to program. It does provide, however, a rational relationship.

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TABLE VI

(C) COMPARISON OF MAXIMUM %  $I_{sp}$  DELIVERED IN SIMILAR ENGINES

<u>Propellants</u>	<u>Max. % <math>I_{sp}</math> Delivered</u>	<u>Reference</u>
RP-1/Liquid Oxygen	92	1
$N_2O_4$ /UDMH	91	4
Hybaline $A_5$ /Liquid Oxygen	85	1
Hybaline $A_5$ / $N_2O_4$	85	4
Hybaline $B_3$ / $N_2O_4$	82	—
Hybaline $A_5$ /90% $H_2O_2$	86	6
Hybaline $B_3$ /90% $H_2O_2$	84	—
$B_5H_9$ / $N_2H_4$	75	7

(C) Hybaline  $B_3$  possesses an inherent instability at temperatures above 60°F. This instability produces negligible changes in composition over a one-year period. Pressure buildup is significant, however, and must be considered in system design.

(U) Hybaline  $B_3$  is compatible with most standard materials used in missile construction. Benzene is a satisfactory solvent for  $B_3$ . Air and moisture must be excluded. Hybaline  $B_3$  is pyrophoric with air of relatively low humidity, and appropriate precautions are necessary.

## CONCLUSIONS.

The conclusions derived from the test program thus far have been:

(C) 1. Delivered performance from both the Hybaline  $B_3$ / $N_2O_4$  and the Hybaline  $B_3$ / $N_2O_2$  (90 wt. %) propellant combinations was low. However, all reported fixings were made using only one type of injection technique. The BN reaction theoretically predicted for the Hybaline  $B_3$ / $N_2O_4$  was not achieved.

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(U) 2. Hybaline B<sub>3</sub> is storable for a period of at least a year. Venting will be necessary for certain applications.

(U) 3. No problems are anticipated in using Hybaline B<sub>3</sub> with the standard materials used in missile construction.

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